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OFFICE OF NAVAL RESEARCH
Contract N00014-89-J-1052
R & J Code 4134036
Technical Report No. 52

CHEMISORPTION OF CARBON MONOXIDE ON THREE METAL SURFACES:

Ni(111), Pd(111) and Pt(111); A COMPARATIVE STUDY

by

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Prepared for Publication

in

J. Phys. Chem.

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) #52			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION ONR		
6c. ADDRESS (City, State, and ZIP Code) Cornell University Baker Laboratory Ithaca, NY 14853-1301			7b. ADDRESS (City, State, and ZIP Code) 800 Quincy Street, Arlington, VA		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Report #52		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Chemisorption of Carbon Monoxide on Three Metal Surfaces: Ni(111), Pd(111) and Pt(111): A Comparative Study					
12. PERSONAL AUTHOR(S) Y.-T. Wong and R. Hoffmann					
13a. TYPE OF REPORT Technical Report #52		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) October 12, 1990	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Chemisorption, Carbon monoxide, Pt, Pd, Ni		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) At one-third coverage of carbon monoxide, a ($\sqrt{3} \times \sqrt{3}$)R30° low energy electron diffraction (LEED) pattern has been observed on Ni(111), Pd(111) and Pt(111). Interestingly, the C-O stretching frequency indicates three completely different adsorption sites; a 2-fold bridge site for Ni(111), a 3-fold site for Pd(111), and an on-top site for Pt(111). As the coverage increases to one-half, a c(4x2) LEED pattern appears. For Ni(111) and Pd(111), the adsorbate seems to prefer the 2-fold site. On Pt(111), half of the chemisorbed CO sits on the on-top site while the other half is located at the 2-fold site. Further increase in coverage results in tilted CO molecules on Pt(111) and adsorption of CO at the on-top site of Ni(111) and Pd(111). To rationalize these observations, we carried out extended Hückel calculations within the tight-binding formalism. Our discussion is augmented by conceptual tools such as density of states and crystal orbital overlap population. We also examine the question of the adequacy of the Blyholder model in describing the adsorbate-surface interaction. 72					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Roald Hoffmann			22b. TELEPHONE (Include Area Code) 607-255-3419		22c. OFFICE SYMBOL

**Chemisorption of carbon monoxide on three metal surfaces:
Ni(111), Pd(111) and Pt(111); A comparative study.**

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Abstract: At one-third coverage of carbon monoxide, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ low energy electron diffraction (LEED) pattern has been observed on Ni(111), Pd(111) and Pt(111). Interestingly, the C-O stretching frequency indicates three completely different adsorption sites; a 2-fold bridge site for Ni(111), a 3-fold site for Pd(111), and an on-top site for Pt(111). As the coverage increases to one-half, a $c(4 \times 2)$ LEED pattern appears. For Ni(111) and Pd(111), the adsorbate seems to prefer the 2-fold site. On Pt(111), half of the chemisorbed CO sits on the on-top site while the other half is located at the 2-fold site. Further increase in coverage results in tilted CO molecules on Pt(111) and adsorption of CO at the on-top site of Ni(111) and Pd(111). To rationalize these observations, we carried out extended Hückel calculations within the tight-binding formalism. Our discussion is augmented by conceptual tools such as density of states and crystal orbital overlap population. We also examine the question of the adequacy of the Blyholder model in describing the adsorbate-surface interaction.

Introduction

Surface science, a subject which lies on the shared border of chemistry, physics and material science, has recently undergone spectacular advances. On the experimental side, the striking development is driven mainly by the invention of new spectroscopic methods such as surface extended X-ray fine structure (SEXAFS) and scanning tunneling microscopy (STM). On the theoretical side, it is powered by better computational techniques and improved computer machinery. Due to its challenging and interdisciplinary nature, and to its plain utility, the field has also caught the attention of many chemists. The growing importance of surface chemistry is undeniable, as reflected by the increasing number of contributions to this area. At the time of writing, the most recent issues of two prime series of monographs in Physical Chemistry, *Advances in Quantum Chemistry* and *Advances in Chemical Physics*, are either partly or completely devoted to this subject.^{1,2}

One of the most extensively studied adsorbates is carbon monoxide. Its interaction with surfaces has constituted the model systems for molecular chemisorption for many years. The reason for this is manifold. CO is the reactant for some important catalytic processes, for example, Fischer-Tropsch synthesis. Secondly it is ubiquitous, binding spontaneously to many surfaces. C-O bond stretching usually gives rise to an intense and sharp infrared absorption peak. From the frequency of this band, the location of the adsorbate at the on-top, two-fold, three-fold or four-fold adsorption site can be deduced. CO also exhibits a rich variety of bonding modes. For Pt(111) only, three adsorption sites have been reported.³ The molecular axis of the chemisorbed carbon monoxide can be parallel, perpendicular, or tilted with respect to the surface.⁴⁻⁶

The interaction between carbon monoxide and metal surface is traditionally described by the Blyholder model involving 5σ to metal forward donation and metal to 2π back-bonding.⁷ This is in accord with frontier orbital theory, for the 5σ and 2π are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively. Ultraviolet photoelectron spectroscopy (UPS) studies for carbon monoxide revealed a shift of the 5σ level relative to the 1π and 4σ levels. The energy shift

has been considered as the evidence for the 5σ being the major participant in the metal-CO bonding.⁸⁻¹¹ This viewpoint is supported by the theoretical work of Anderson et al. on Pt(111).¹² Cluster calculations by Bagus, Nelin and Bauschlicher, however, indicated that the 2π orbitals are much more important. They attributed the increase in binding energy of the 5σ , with respect to the gas-phase value, to electrostatic effect.¹³ Effective core potential calculations on small metal clusters suggested that the 5σ -Pd interaction is actually repulsive.¹⁴ Moreover, the position of the 5σ seems to be insensitive to the crystallographic orientation or the nature of the surface.^{11,15} Motivated by these peculiar observations, Rogozik et al. performed some inverse photoemission experiments on the stepped Pd(111) and Ru(001) surface. In both cases, they found that the empty 2π states for the more tightly-bound adsorbate are about 0.8 eV closer to the Fermi energy, indicating the predominant importance of the back-bonding in CO chemisorption.¹¹ Frank et al., however, demonstrated that the position of these unoccupied states is mainly determined by lateral interactions between adsorbate molecules. The position of this band can be taken as a direct measure of the strength of back-bonding only at low CO coverage.¹⁶ There are some speculations that besides the HOMO and LUMO, the 4σ may be involved intimately in metal-CO bonding.^{17,18} Finally, a paper addressing to the inadequacy of the Blyholder model has appeared.¹⁵

For a research group specializing on orbital interactions, these controversies represent a big apple whose temptation cannot be easily resisted. Although the extended Hückel method has a lot of limitations, analysis of orbital interaction by this technique seems to be moderately reliable. In contrast to other methods whose arguments are either based on the energy shifts of the adsorbate orbitals or the mixing of the metal orbitals with those of carbon monoxide, we can actually determine the contribution of each orbital of the adsorbate to the carbon-metal bond. In this way, a more direct and detailed assessment of the relative significance of the 4σ , 5σ and 2π may be achieved. There is, nevertheless, another incentive for our work.

Chemists are interested not only in the properties of individual atoms, molecules or compounds but also periodic trends, isolobal analogies, homologous series, etc. The qualitative correlation and systematization of the properties of a group of chemical entities is

at least as important as the quantitative, accurate determination all the characteristics of each species.¹⁹ We stress, however, that qualitative and quantitative considerations in chemistry are inseparable. Before meaningful correlation and systematization, which will inevitably lead to prediction, an extensive, reliable, quantitative database must be available. There have been a wealth of experimental and theoretical findings for the adsorption of CO on Ni(111), Pd(111) and Pt(111). Stimulated by a challenge from Norman Sheppard, we try in this paper to understand why carbon monoxide exhibits completely different chemisorptive behavior on the above three metal surfaces.

The organization of this work is as follows. The chemisorption of CO at one-third coverage is first investigated in the following order: Pt(111), Pd(111) and Ni(111). We then analyze briefly the effect of adsorbate-adsorbate interaction at one-half coverage. There are two different types of three-fold sites on the (111) surface of a face-centered cubic structure: the hcp hollow site, which has a second-layer metal atom under it, and the fcc hollow site, which does not have one. Apart from a small energetic difference, the bonding in these two three-fold sites is extremely similar. It is sufficient to single out one of them in our discussion. Hereafter, "three-fold site" refers to the fcc hollow site unless otherwise specified. For compactness, the on-top, two-fold and three-fold site of Pt(111) will be abbreviated as Pt(on-top), Pt(2-fold), and Pt(3-fold), respectively. Similar conventions apply to the other two metal surfaces. As a compromise between speed and accuracy, three-layer slabs serve as models for the metal surfaces. The adsorbate molecules are put on one-side of the two-dimensional slabs only. This covered layer will be referred to hereafter as the surface layer. We reemphasize that the extended Hückel method has only limited reliability. Its strength is transparency, not accuracy. The main objective of this work is to provide a rough, comparative picture of chemisorption of carbon monoxide on the three metal surfaces.

Throughout his paper, two conceptual tools, density of states (DOS) and crystal orbital overlap population (COOP) curve, are utilized extensively to shed more light on the adsorbate-surface interaction. The DOS curve is a plot of the number of orbitals per unit volume per unit energy as abscissa, versus energy as ordinate. The COOP curve is a graph

of the overlap-population-weighted density of states versus energy. Integration of the COOP curve up to the Fermi energy gives the total overlap population.²⁰ Further computational details are given in the Appendix. Equipped with means and motivation, we begin our journey into the comparative study of the adsorption of carbon monoxide on the three surfaces mentioned above.

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Chemisorption of CO on Pt(111)

The amount of experimental and theoretical work devoted to the adsorption of CO on Pt(111) is phenomenal. Yet many aspects remain controversial.

At one-third coverage of carbon monoxide ($\theta = 1/3$), a diffuse $(\sqrt{3} \times \sqrt{3})R30^\circ$ low energy electron diffraction (LEED) pattern can be observed. The C-O stretching frequency suggested that up to this coverage, only the on-top site was occupied.³ As θ increases to $1/2$, a $c(4 \times 2)$ surface structure is formed, in which one-half of the CO molecules are located at the on-top site while the other half adsorb on the 2-fold site.²¹ These experimental results are supported by Monte Carlo simulation.²² More recent study by infrared reflection-absorption spectroscopy (IRAS), however, indicated that the 2-fold site begins to be populated when θ is around 0.2 to 0.3.²³ At a coverage higher than 0.6, the terminally bonded adsorbate molecules are tilted 6° off the normal to the surface.⁶

The adsorption behavior of CO seems to be strongly dependent on surface conditions. An infrared absorption peak near 1810 cm^{-1} has been taken as evidence for the occupation of the three-fold site.³ By using the same Pt(111) sample but different cleaning procedure and spectrometer, no signal near this frequency can be observed.²⁴ The most recent study of this adsorption site, interestingly, occurred in electrolyte solution.²⁵ Yet the reported C-O stretching frequency, $1770\text{-}1785 \text{ cm}^{-1}$, differs slightly from the previous assignment. To our knowledge, there seems to be no crystallographic data for organometallic compounds with a μ_3 -CO capping three platinum atoms.

Concerning the energetics, the following is known: The binding energy at the on-top site is about 1.4 eV and is essentially coverage-independent.²⁶⁻²⁸ At low coverage, Bradshaw et al. estimated that the on-top site is 60 meV more stable than the 2-fold site.²¹ Froitzheim and Schulze, however, deduced a value of about 0.3 eV.²⁸

This brief review is not meant to confuse or discourage the reader, but to reflect our incomplete and fragmentary understanding of surface phenomena. Compared with X-

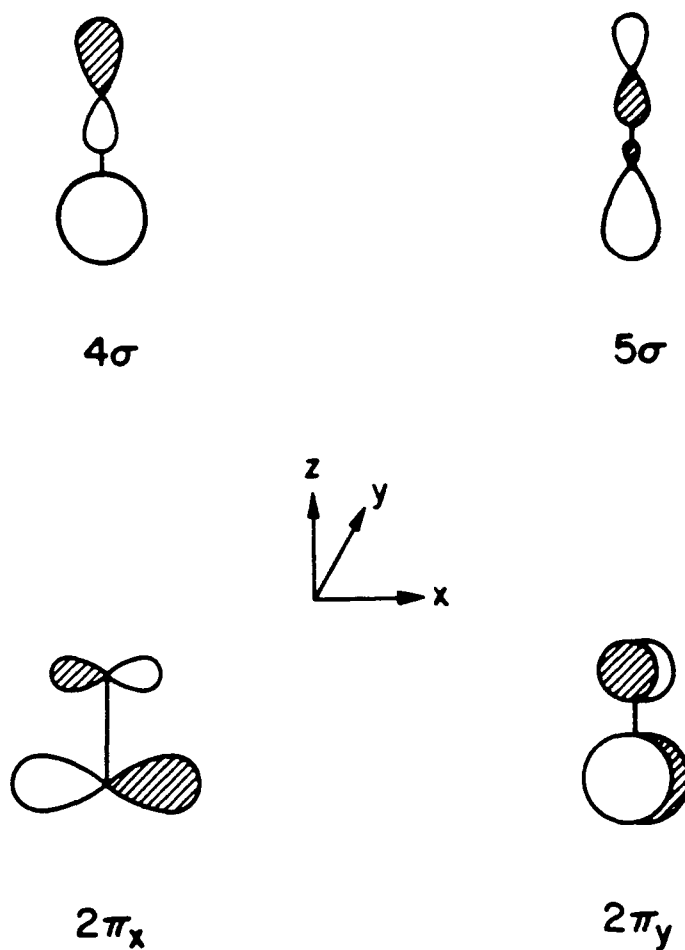
ray diffraction used for the bulk, no surface structural probes have matured to the point where straightforward use of any one of them will always give equally detailed and reliable results. Pioneers in surface science frequently have to push their techniques to the limit. Contradictory results are the rule rather than the exception. Nature is not particularly merciful in this regard either. Extremely complicated situations can arise from deceptively simple cases. Significant breakthroughs often come from an unexpected and entirely different direction. The story of the elucidation of the Si(111) 7x7 surface reconstruction is a prime example of the harsh reality (and also a great triumph).

The Pt(111)-c(4x2)-2CO surface structure has been investigated in detail by dynamical LEED. The C-O bond distance seems to be the same 1.15 Å for both adsorption sites. The C-Pt bond lengths are 1.85 and 2.08 Å, respectively, for the on-top and 2-fold bridge site.²⁹ The corresponding values obtained by the atomic superposition and electron delocalization (ASED) theoretical technique are 2.05 and 2.16 Å, respectively.¹² For organoplatinum(0) carbonyls, the Pt-C distances usually average around 1.84 to 1.92 Å for terminal CO and 1.92 to 2.07 Å for μ_2 -CO.³⁰

Considering all the above experimental and theoretical information, we reach the following geometrical decisions. The Pt-C bond lengths for the on-top and 2-fold site are taken from the LEED data (1.85 and 2.08 Å, respectively). Since the experimental data for the exact geometry of the adsorbate at the 3-fold site is not available, we adopt the theoretical Pt-C bond length (2.23 Å) from ASED.¹² The C-O and the nearest Pt-Pt distances are set to 1.15 and 2.77 Å respectively. The reason we have to choose the separations is that we cannot rely on the extended Hückel method to give us correct bond lengths. The valence state ionization potentials (H_{ii}) for the platinum are refined by charge iteration on the c(4x2)-2CO surface structure (with half of the CO being linearly bonded while the other half is 2-fold bridged) until self-consistency is attained.

On-top, two-fold site, and three-fold on Pt(111) at one-third coverage

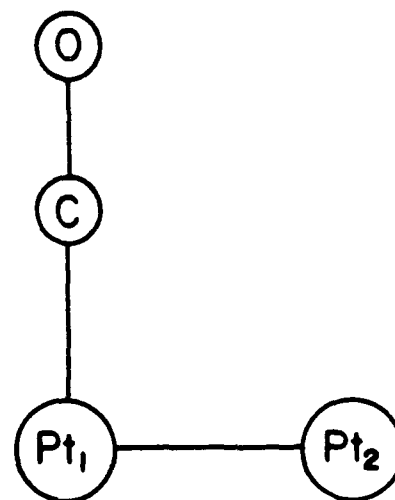
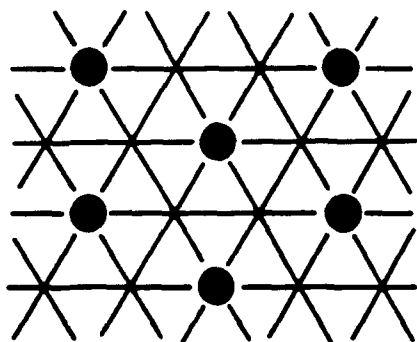
The four frontier orbitals of carbon monoxide, those which are believed to be important in bonding with the metal surfaces, are sketched in 1. A CO molecule in the gas



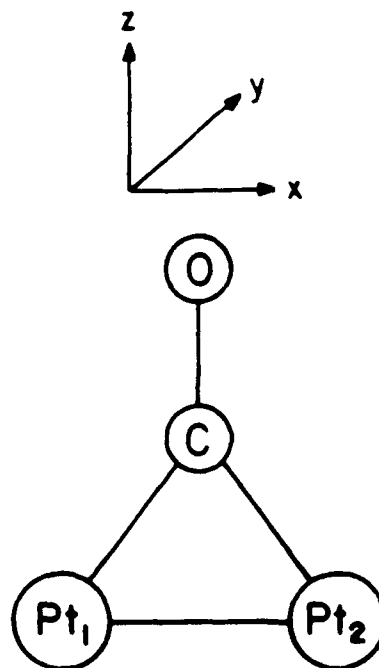
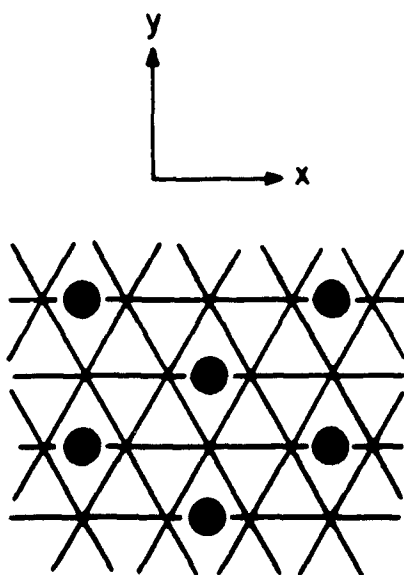
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phase has an equilibrium bond distance of 1.13 Å. The calculated overlap population (OP) is 1.245. For the bare Pt(111) surface, the OP between surface Pt-surface Pt, surface Pt-bulk Pt and bulk Pt-bulk Pt are 0.176, 0.141 and 0.151, respectively. These values are reference points for subsequent calculations on the chemisorbed Pt-CO system.

Top views of the three $(\sqrt{3}\times\sqrt{3})R30^\circ$ structures, together with the numbering of the metal atoms for Pt(on-top), Pt(2-fold), and Pt(3-fold) are sketched in 2, 3 and 4. The solid circles represent the adsorbate molecules, which are perpendicular to the surface. At the 2-fold site $2\pi_x$ is defined to be parallel to, $2\pi_y$ perpendicular to, the nearest

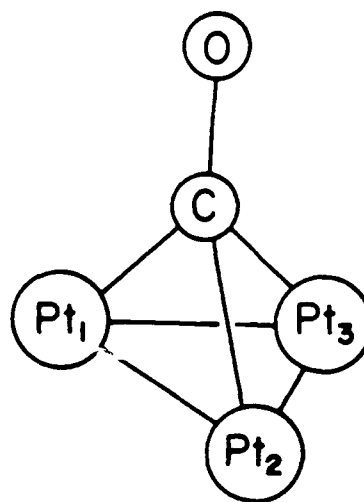
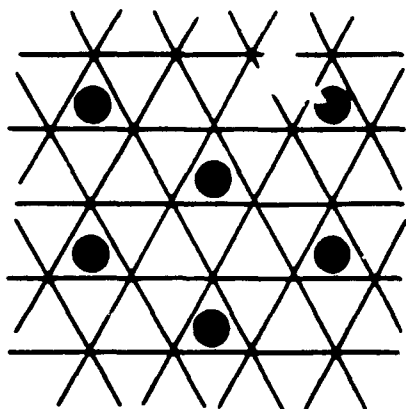


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4

metal-metal bond. Since the adsorption of carbon monoxide on metal surfaces has been studied extensively, we shall concentrate on areas that have not been sufficiently explored. For example, the degeneracy of 2π is lifted at the 2-fold site 3. $2\pi_x$ and $2\pi_y$ are no longer equivalent. Their individual roles on adsorbate-surface interaction, however, have seldom been assessed separately. At Pt(on-top) and Pt(3-fold), the C_3 rotational axes passing through the adsorbate molecules ensure that $2\pi_x$ and $2\pi_y$ are symmetry-equivalent.

Selected computed bonding information is collected in Table 1. The C-Pt OP in this table for Pt(2-fold) is actually the sum of the OP of two equivalent bonds: C-Pt₁ and C-Pt₂. For the 3-fold site, it is the total of three C-Pt bonds. Notice that at this adsorption site there is severe weakening of three Pt-Pt bonds at the surface per adsorbate molecule. Similar summations have been performed for the OP of the four frontier orbitals.

Table 1 here

Strictly speaking, the overlap population between a metal atom and a particular

Table 1. Selected Bonding Information at Pt(on-top), Pt(2-fold) and Pt(3-fold).

	on-top	2-fold	3-fold
binding energy (eV)	2.778	2.651	2.489
C-O OP	1.136	1.093	1.091
C-Pt OP	0.842	0.910	0.963
Pt ₁ -Pt ₂ OP	0.134	0.074	0.095
4σ-Pt OP	0.141	0.123	0.110
5σ-Pt OP	0.491	0.457	0.472
2π _x -Pt OP	0.115	0.264	0.203
2π _y -Pt OP	0.115	0.089	0.203
electron occupation of 4σ	1.844	1.839	1.847
electron occupation of 5σ	1.538	1.499	1.488
electron occupation of 2π _x	0.189	0.371	0.283
electron occupation of 2π _y	0.189	0.186	0.283
Net charge on CO	+0.241	+0.106	+0.101

fragment molecular orbital of CO molecule consists of two parts, the metal-carbon OP and the metal-oxygen OP. We are primarily interested in the carbon-metal bonding. More importantly, the overlap population for two different pairs of atoms should not be added together. Although the metal-O OP's would be very small, we have separated the above two components. All the COOP curves and overlap populations in this paper contain the carbon-metal contributions only.

The four frontier orbitals 4σ , 5σ , $2\pi_x$ and $2\pi_y$ account for nearly all the C-Pt OP. Four minus their total electron occupation also gives roughly the net charge of the adsorbate. Hence, there seems to be little doubt that these molecular orbitals are responsible for most of the metal to carbon monoxide bonding. The electron populations indicates that the 4σ and 5σ to metal forward donation of electron greatly outweigh the back-donation to the 2π pair; the net charge of the adsorbate is positive.

The projected OP's in Table 1 reveal some interesting features. The 4σ is probably not a spectator orbital.^{17,18} Take the on-top site as an example. Its contribution to the C-Pt OP is greater than that of $2\pi_x$ or $2\pi_y$. The overlap between 4σ with the s , p_z and d_{z^2} orbital of Pt_1 is 0.321, 0.413 and 0.159, respectively. In all three cases, the 5σ is the most important bonding orbital. Note its large down-shift in energy, its obvious mixing with metal d orbitals (best seen by following the integration in the energy range between -7 and -11 eV); and the mixing that pushes a substantial part of its density of states to high energy. The projected DOS and COOP curve for 4σ and 5σ at Pd(on-top) are displayed in Figure 1 and 2. About 8% of the DOS of 4σ is in resonance with that of 5σ . Similar mixing of orbitals also occurs for the two other adsorption sites.

Figure 1 and 2 here

Since the degree of depopulation of 4σ and 5σ , and the population of $2\pi_x$ and $2\pi_y$ provide a rough measure of the strength of their interactions with the surface, we may compare the relative strength of the bonding of these four orbitals to the metal at various

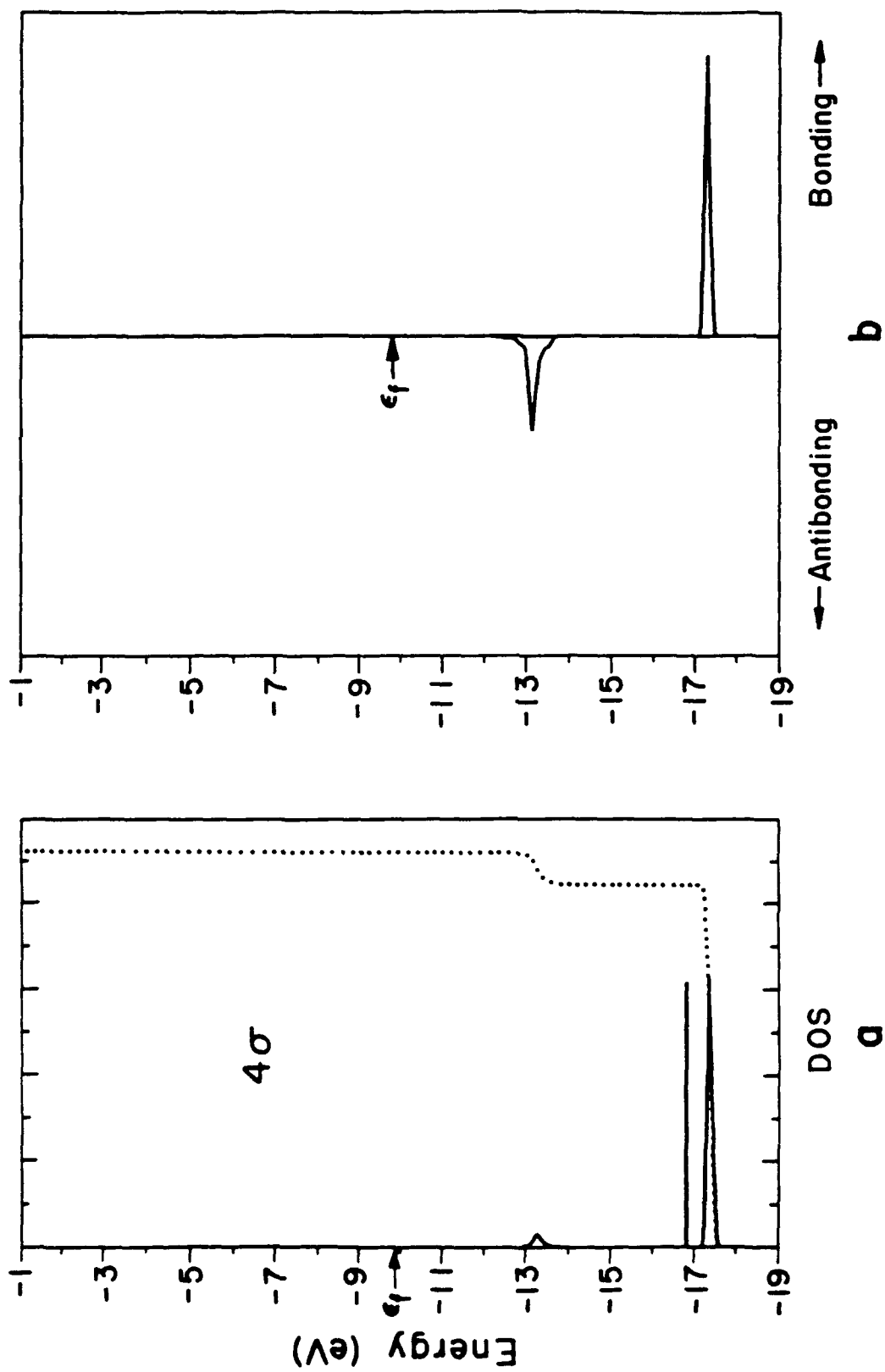


Figure 1. a) DOS of 4d at Pt(on-top). The horizontal line displays the position of the 4s in a free undistorted CO molecule.
b) 4s-Pt₁ COOP curve.

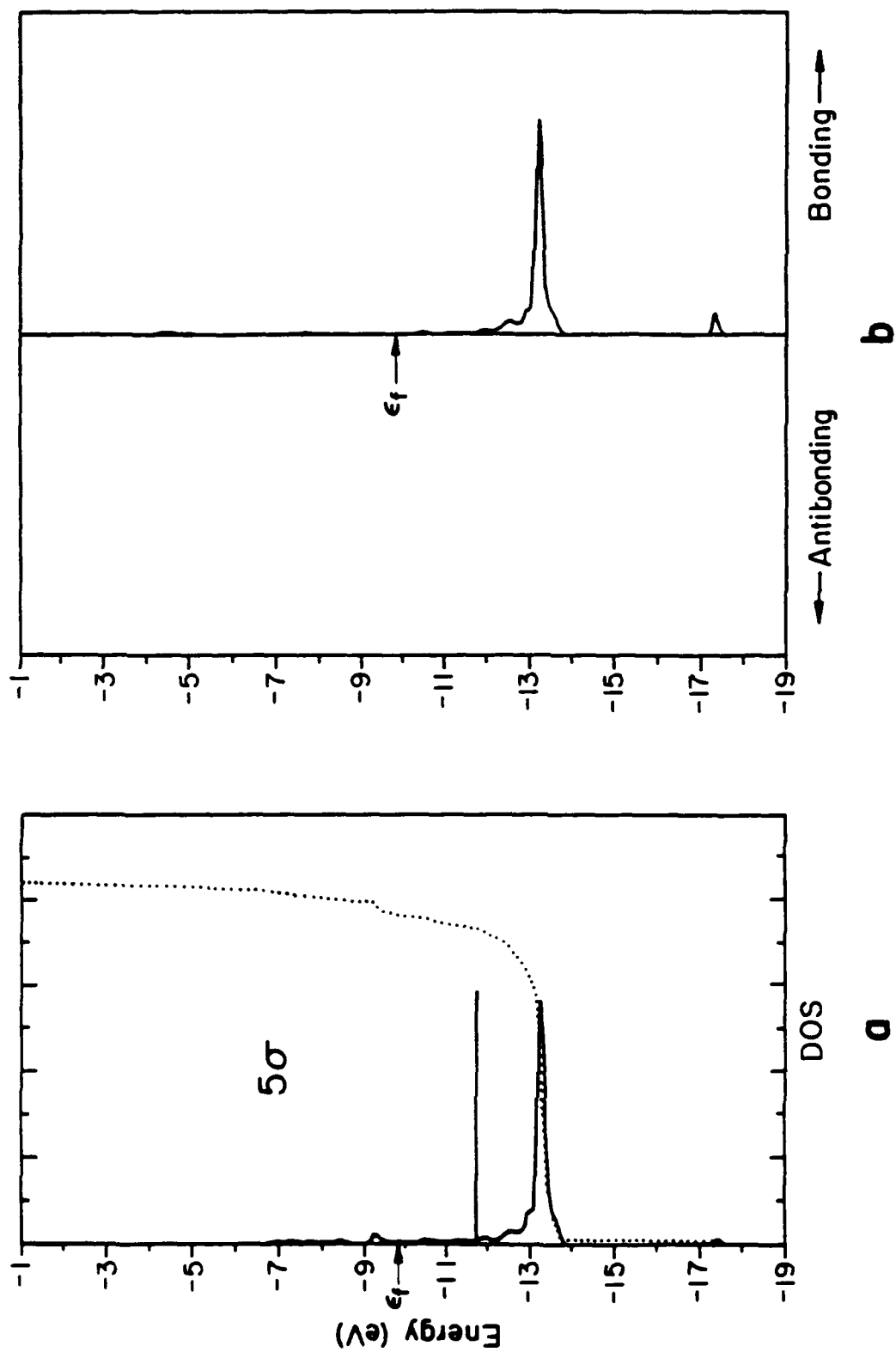


Figure 2. a) DOS of 5σ at Pt(on-top). The horizontal line displays the position of the 5σ in a free undistorted CO molecule.
b) 5σ-Pt₁ COOP curve.

adsorption sites by their electron occupancies. Another indicator of interaction is the DOS. The electron populations in Table 1 indicate that the strength of the 4σ -surface interaction is essentially the same for all adsorption sites. In fact, the DOS of 4σ at Pt(on-top), Pt(2-fold) and Pt(3-fold) are almost identical. The electron population and DOS of the 5σ show similar trends. In Table 2 and 3, a more detailed picture for the interaction of these two frontier orbitals with the metal surface is presented.

Table 2 and 3 here

In these two tables, the total OP's between the 4σ or 5σ with the nearest surface orbitals are listed. When there are more than one such surface orbitals, the total is given. Although at Pt(on-top) the overlap between 4σ and the p_z orbital of Pt_1 is greatest, it is the s orbital, with its better energy matching for interaction, that makes the largest contribution to the 4σ - Pt_1 OP. The same is true for the 5σ orbital. The 5σ interacts not only with the empty s and p surface orbital, but there seems to be significant bonding with the d_{z^2} bands as well. The 5σ - d_{z^2} interaction has been noted previously by our group³¹ and other researchers.^{17,32} As we move across the series: Pt(on-top), Pt(2-fold) to Pt(3-fold), the interaction between the 5σ and d_{z^2} decreases. However, more and d orbitals can mix into the 5σ due to removal of a symmetry constraint. The consequence is that the percentage contribution of all the d orbitals to the Pt- 5σ bonding among various adsorption sites are essentially constant, around 22%.

If we consider the surface s and p band as one level, the sigma bonding between the adsorbate and the surface at Pt(on-top) may be described by a four-level interaction in 5. From the orbital interaction concepts learned in molecular chemistry, one would expect the lowest level to be Pt- 4σ and Pt- 5σ bonding, while the second level should be Pt- 4σ antibonding but Pt- 5σ bonding. These characteristics are nicely illustrated by the COOP curves in Figure 1 and 2. The antibonding peak of the COOP curve in the first figure also serves as evidence for the 4σ - 5σ mixing. The other two antibonding levels are above the

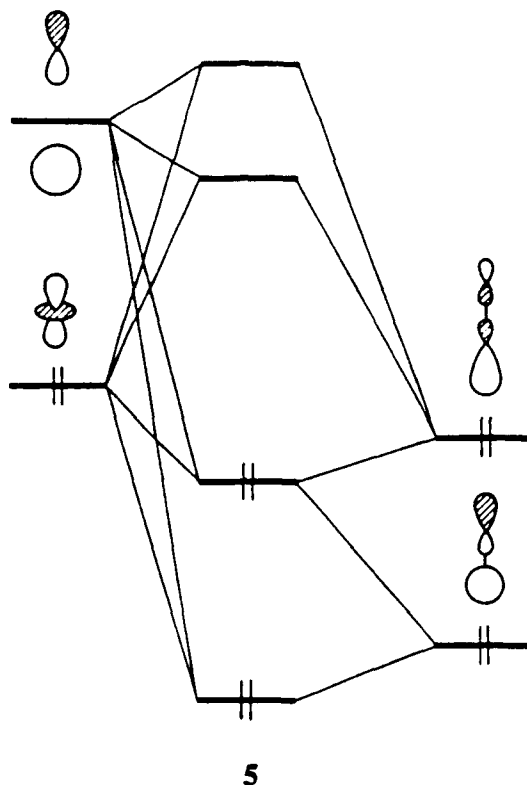
Table 2. Overlap Populations Between the 4σ and the Nine Surface Bands.

orbital	on-top	2-fold	3-fold
s	0.078	0.073	0.069
p_x	0	0.003	-0.001
p_y	0	0	-0.001
p_z	0.044	0.028	0.026
$d_{x^2-y^2}$	0	0.001	0.001
d_{z^2}	0.020	0.003	0.002
d_{xy}	0	0	0.001
d_{xz}	0	0.001	0.006
d_{yz}	0	0	0.006

Table 3. Overlap Populations Between the 5σ and the Nine Surface Bands.

orbital	on-top	2-fold	3-fold
s	0.219	0.219	0.231
p_x	0	0.057	0.033
p_y	0	0	0.033
p_z	0.159	0.080	0.075
$d_{x^2-y^2}$	0.000	0.016	0.011
d_{z^2}	0.113	0.008	0.001
d_{xy}	0	0	0.011
d_{xz}	0	0.077	0.038
d_{yz}	0	0	0.038

Fermi energy and hence are empty. Similar interaction diagrams for the other two sites may be constructed from the computed results in Table 2 and 3.



Although $2\pi_x$ and $2\pi_y$ account for less than 40% of the C-Pt OP (see Table 1), the differences in their electron populations among the three adsorption sites are much larger than those of the sigma counterparts. Thus the π orbitals may still play a decisive role in site preference. Further investigation of the projected OP in Table 4 and 5 seems to be in order.

Table 4 and 5 here

At Pt(on-top), $2\pi_x$ and $2\pi_y$ are locally orthogonal to the nearest surface s, p_z and d_{z^2} orbitals. Their bonding with the metal may be viewed basically as simple two-level interactions, that is, $2\pi_x$ with d_{xz} and $2\pi_y$ with d_{yz} . Such is not the case for Pt(2-fold). At

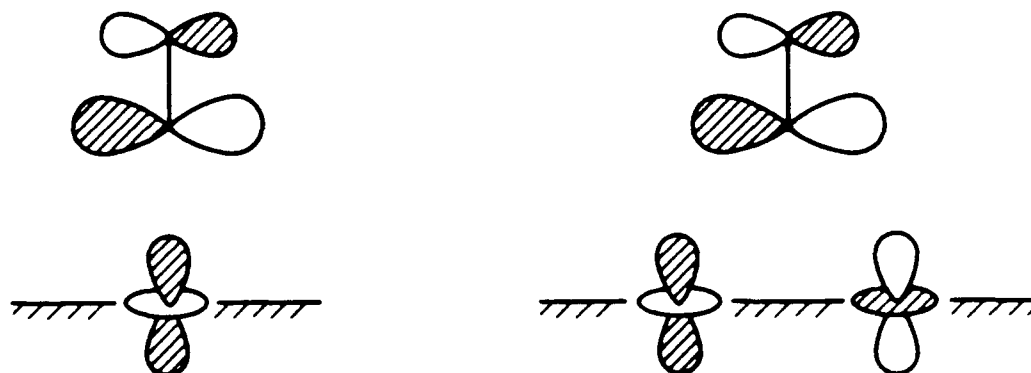
Table 4. Overlap Populations Between the $2\pi_x$ and the Nine Surface Bands.

orbital	on-top	2-fold	3-fold
s	0	0.069	0.047
p_x	0.010	0.003	0.005
p_y	0	0	0.005
p_z	0	0.029	0.016
$d_{x^2-y^2}$	0	0	0.002
d_z^2	0	0.094	0.038
d_{xy}	0	0	0.019
d_{xz}	0.105	0.069	0.040
d_{yz}	0	0	0.033

Table 5. Overlap Populations Between the $2\pi_y$ and the Nine Surface Bands.

orbital	on-top	2-fold	3-fold
s	0	0	0.047
p _x	0	0	0.005
p _y	0.010	0.096	0.005
p _z	0	0	0.016
d _{x²-y²}	0	0	0.019
d _{z²}	0	0	0.038
d _{xy}	0	0.033	0.002
d _{xz}	0	0	0.033
d _{yz}	0.105	0.046	0.040

this adsorption site, there are effective overlaps between $2\pi_x$ and the above three surface bands, 6. The result is remarkable. The electron population of $2\pi_x$ is almost doubled,



6

relative to the on-top case, or $2\pi_y$. In the on-top site, it contributes an OP of 0.115 to one Pt-C bond only, while in the 2-fold site, the OP is 0.132 to each of the two Pt-C bonds. The d bands account for more than 88% of the $2\pi_x$ -Pt OP at the on-top site, but less than 62% when the adsorbate is located at the 2-fold site. Notice that by local symmetry, $2\pi_x$ can only interact extensively with the s and p_z orbitals that are Pt_1 - Pt_2 antibonding. These surface orbitals should be mainly empty in the case of the free surface. Hence, the bonding between the $2\pi_x$ and these surface orbitals does not fall into the category of either the forward donation or back-donation of the Blyholder model. The symmetry constraints between $2\pi_y$ and the above three surface bands have not been relaxed even at Pt(2-fold). There is no drastic change in its electron occupancy and the d bands still contribute about 88% of the $2\pi_y$ -metal OP. The Pt- $2\pi_y$ OP is only 34% of that of the $2\pi_x$.

The difference between these two orbitals can be illustrated by the DOS curves in Figure 3. For comparison, the DOS of these two frontier orbitals at Pt(on-top) and Pt(3-

fold) are displayed in the same figure. Note the most obvious feature of these 2π DOS, contributions, namely their substantial dispersion, indicative of extensive interaction.

Figure 3 here

What happens when the carbon monoxide molecules are moved from Pt(2-fold) to Pt(3-fold) ? The projected OP's in Table 4 and 5 indicate that $2\pi_x$ and $2\pi_y$ become degenerate again. The interactions of $2\pi_x$ with the s, p_z and d_{z^2} decrease substantially, as reflected by the reduction in its electron population. The opposite occurs for $2\pi_y$. At this adsorption site, the d orbitals account for about 64% of the OP between the 2π pair and the metal. Moreover, the total electron occupancy of the 2π pair is largest at Pt(3-fold), suggesting probably the strongest 2π to metal bonding.

In summary, the strength of the bonding between 4σ and 5σ and the metal surface changes only slightly among various adsorption site, while the $2\pi_x$ and $2\pi_y$ interactions favor a higher coordination site. The difference between Pt(2-fold) and Pt(3-fold) is, however, marginal. This bonding effects are counterbalanced by more and more weakening of the C-O and the Pt-Pt bonds at the surface. The net result is that the binding energies at various adsorption sites are very similar. It appears that in these calculations the bond-weakening may take precedence. Thus Pt(on-top) appears to be the most stable site. The balance, nevertheless, seems to be extremely delicate. If the differential weakening of the metal-metal bonds among the three adsorption sites were much smaller, then the table may turn.

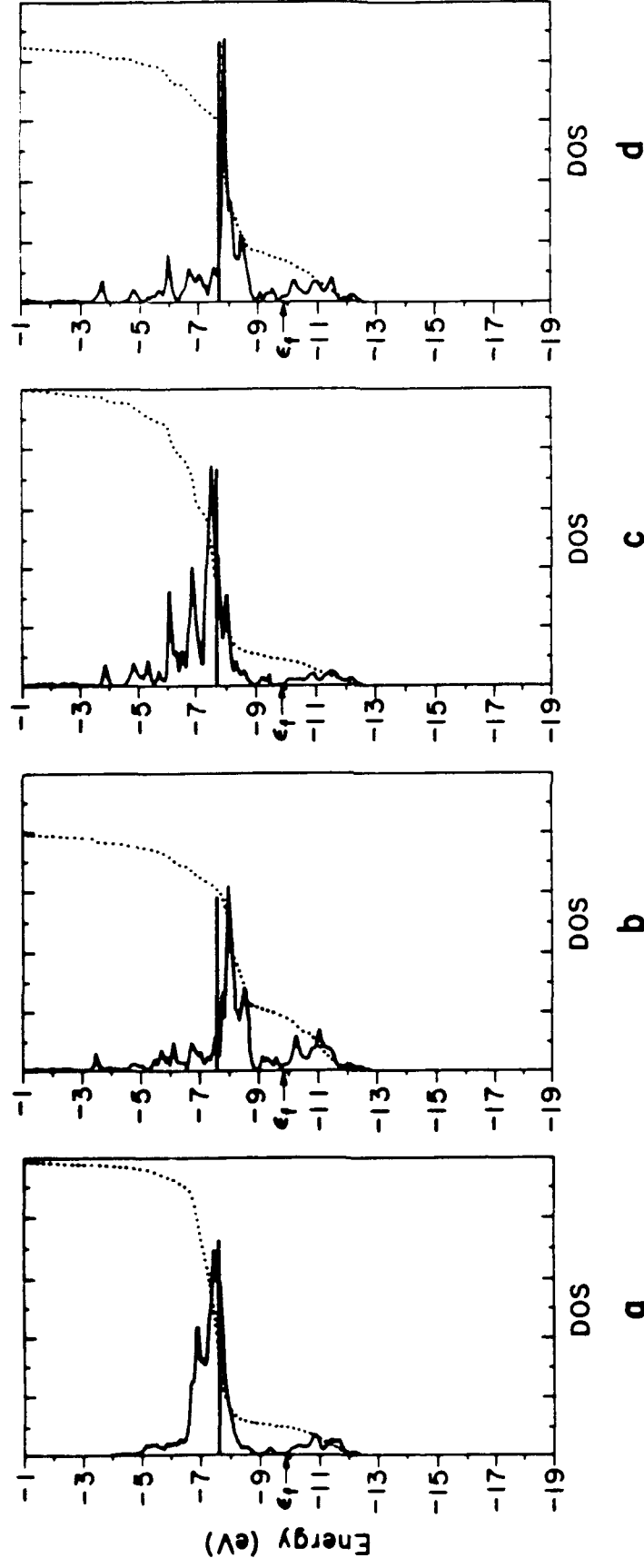


Figure 3. a) DOS of $2\pi_x$ or $2\pi_y$ at Pt(on-top).
b) DOS of $2\pi_x$ at Pt(2-fold).
c) DOS of $2\pi_y$ at Pt(2-fold).
d) DOS of $2\pi_x$ or $2\pi_y$ at Pt(3-fold).

Chemisorption of CO on Pd(111)

The chemisorption energy of CO on Pd(111) remains constant at about 1.47 eV up to a coverage of one-third, possibly signalling a single adsorption site. This observation is supported by other experimental data. The C-O stretching frequency and the dynamical LEED both suggested that only the 3-fold sites are occupied in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure.³³⁻³⁵ Secondary ion mass spectrometry, however, favored a mixture of domains of 2-fold and 3-fold bridged adsorbate.³⁶

At one-half coverage, a $c(4\times 2)$ ordered surface structure is formed in which all the CO molecules seem to be located at the 2-fold site. Further increase in coverage results in terminally bonded adsorbate.³³

From the experimental work of Somorjai et al., the C-O and Pd-C bond length in the Pd(111)- $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure have been found to be 1.15 and 2.05 Å, respectively. The fcc hollow site appears to be the preferred adsorption site.³⁵ On Pd(100), where the CO molecules populate the 2-fold site only, the experimental C-O and Pd-C bond length are 1.15 and 1.93 Å, respectively.³⁷ In organopalladium carbonyls, the Pd-C distances generally range from 1.97 to 2.12 Å for μ_2 -CO, and 2.02 to 2.32 Å for μ_3 -CO.³⁸⁻⁴¹ In contrast to the platinum and nickel carbonyls, organopalladium compounds with terminal CO are rare and less stable. A few have been isolated³⁰ but there seems to be no relevant crystallographic data. Although there is no direct experimental guidance for Pd(on-top), the metal-C bond should be (a) much shorter than 1.93 Å; (b) much longer than that in Ni(on-top) (which is about 1.71 Å) and (c) similar to that in Pt(on-top). Taking all these factors into account, the Pd-C bond length for Pd(on-top), Pd(2-fold) and Pd(3-fold) are chosen to be 1.82, 1.93 and 2.05 Å, respectively, while the C-O bonds are fixed at 1.15 Å. The H_{ii} 's of palladium are determined by charge iteration of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure with all the CO molecules located at the 3-fold site.

On-top, two-fold, and three-fold site on Pd(111) at one-third coverage

A casual comparison between Table 1 and Table 6 reveals the similarities of adsorbate-surface interaction on Pt(111) and Pd(111). It is also well-known that the chemistry of palladium is much closer to that of platinum than nickel.³⁰ The 5σ -Pd interaction seems to be attractive. Again the electron population of $2\pi_x$ is highest at the 2-fold site. On going from Pd(on-top) to Pd(2-fold), the electron population of $2\pi_y$ actually increases by 0.029, suggesting possibly a strengthening in the metal- $2\pi_y$ bonding. For Pt(111), the $2\pi_y$ electron occupation decreases slightly (Table 1). As we shall see in Table 7, the same trend is observed on Ni(111), except that the corresponding increase is much larger, about 0.065. Thus, on Pd(111) and Ni(111) both $2\pi_x$ and $2\pi_y$ prefer the 2-fold site to the atop site.

Table 6 here

For the bare Pd(111) slab, the surface Pd-surface Pd OP is computed to be 0.061. The metal-metal OP in Table 6 thus indicates little bond weakening at the surface. The LEED results also point to an unreconstructed Pd(111) substrate even when the CO molecules are located at the 3-fold site.³⁵ Moreover, the Pd-Pd bond weakening seems to be the same for the three adsorption sites. This is important, for the adsorbate-surface interaction may dominate and the adsorption site where the coordination number of the adsorbate is highest may become most stable.

The LEED results strongly favor the fcc hollow site over the hcp site.³⁵ Unfortunately, the energy preference is computed to be only 6 meV, which is, of course, too small to be significant. There has been some experimental evidence for the co-existence of the carbon monoxide at the fcc and hcp hollow site on Ni(111) at low coverage. (The corresponding energy difference on the latter surface is calculated to be 1 meV.) It would be interesting to understand why the adsorbate molecules occupy the fcc hollow sites preferentially on Pd(111) but not Ni(111). Our rough computations certainly cannot

Table 6. Selected Bonding Information at Pd(on-top), Pd(2-fold) and Pd(3-fold).

	on-top	2-fold	3-fold
binding energy (eV)	2.306	2.881	2.946
C-O OP	1.179	1.150	1.144
C-Pd OP	0.691	0.784	0.861
Pd ₁ -Pd ₂ OP	0.057	0.057	0.057
4σ-Pd OP	0.120	0.120	0.120
5σ-Pd OP	0.453	0.445	0.474
2π _x -Pd OP	0.069	0.169	0.150
2π _y -Pd OP	0.069	0.078	0.150
electron occupation of 4σ	1.871	1.850	1.850
electron occupation of 5σ	1.572	1.559	1.538
electron occupation of 2π _x	0.092	0.210	0.179
electron occupation of 2π _y	0.092	0.121	0.179
Net charge on CO	+0.368	+0.253	+0.245

provide a satisfactory explanation for energy differences in the range of several millielectron-volts. Hence the resolution of this puzzle awaits more sophisticated theoretical studies.

Another factor that may stabilize the 2-fold and 3-fold site relative to the on-top site is to the strengthening of the bonding of the $2\pi_x$ and $2\pi_y$ to the surface. This seems to be the case when carbon monoxide molecules are put on Ni(111).

Chemisorption of carbon monoxide on Ni(111):

Early studies suggested that up to a coverage of one-half only the 2-fold sites are occupied.⁴²⁻⁴⁴ This simple picture of chemisorption has been challenged recently by IRAS and high resolution electron energy loss scattering (HREELS). The C-O stretching frequencies obtained by these techniques revealed a much more complicated situation.^{45,46} At low coverage, only the 3-fold sites are populated.⁴⁷ With increase in coverage, a continuous conversion from the 3-fold to 2-fold site occurs. This transformation is complete when θ is about 0.16. Terminally bonded CO can be observed whenever θ is greater than 0.3, but with one exception. At one-half coverage, only 2-fold bridged CO molecules exist.^{46,48}

Three ordered LEED patterns have been reported, namely the $(\sqrt{3}\times\sqrt{3})R30^\circ$ at $\theta = 1/3$, the $c(4\times 2)$ at $\theta = 1/2$ and the $(\sqrt{7}/2\times\sqrt{7}/2)R19.1^\circ$ at $\theta = 0.57$. In the first two surface structures, only the 2-fold sites are occupied. For the last one, in addition to the bridging CO, one-quarter of the adsorbate molecules are in the terminal positions.^{42,43,49,50}

The Ni-C and C-O bond length in the Ni(111)- $(\sqrt{3}\times\sqrt{3})R30^\circ$ -CO system have been determined by normal photoelectron diffraction (NPD) to be 1.78 ± 0.03 and 1.13 Å, respectively.⁵¹ For the surface structure Ni(100)- $c(2\times 2)$ -CO, in which only the on-top sites have been populated, the Ni-C distance is about 1.71 Å.⁵¹⁻⁵⁴ In organonickel carbonyls, the Ni-C bonds are usually bracketed in the domain of 1.69 to 1.86 Å for terminal CO, 1.83 to 1.98 Å for μ_2 -CO and 1.89 to 2.03 Å for μ_3 -CO.^{30,55-57} With these experimental data in mind, the Ni-C bond lengths are taken to be 1.71 , 1.81 and 1.96 Å for Ni(on-top), Ni(2-fold) and Ni(3-fold) respectively. The C-O and Ni-Ni bond lengths are kept fixed at 1.13 and 2.49 Å for all adsorption sites. The valence state ionization potentials of the nickel are obtained by charge iteration of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ system using the NPD results.

On-top, two-fold, and three-fold site on Ni(111) at one-third coverage

The bonding information for CO on various adsorption sites of Ni(111) is listed in Table 7. The total electron occupancy of the $2\pi_x$ and $2\pi_y$ on this surface is greater than the degree of depopulation of 4σ and 5σ . The net charge of the adsorbate is thus negative. If we compare the same adsorption site among the three metal surfaces, the electron populations of the $2\pi_x$ and $2\pi_y$ are highest on Ni(111), signalling probably the strongest metal- π back-bonding. Similar to Pt(111), the metal-metal bond-weakening is substantial and increases significantly as we pass along the series: Ni(on-top), Ni(2-fold) and Ni(3-fold). The compromise between significant bond-weakening at the surface and strong π -metal interaction seems to favor the 2-fold site, but only marginally so with respect to the 3-fold site.

Table 7 here

So far we have concentrated on the metal-carbon monoxide bonding. How about the weakening of the C-O bond? In the Blyholder model, the occupation of the 2π pair is the major source of bond-weakening. Since this bond does not lengthen after adsorption on Ni(111), the nature of the C-O bond-weakening on this surface needs to be examined.

Table 8 lists the contributions of $2\pi_x$ and $2\pi_y$ to the C-O OP. Totally, they account for about 81, 72 and 73% of the decrease in the OP for Ni(on-top), Ni(2-fold) and Ni(3-fold) respectively. Hence the filling of the two 2π orbitals is responsible for most, but not all, of the bond-weakening. The rest is mainly due to depopulation of 4σ and 1π .

Table 8 here

Table 7. Selected Bonding Information at Ni(on-top), Ni(2-fold) and Ni(3-fold).

	on-top	2-fold	3-fold
binding energy (eV)	2.762	3.335	3.216
C-O OP	1.105	1.016	1.009
C-Ni OP	0.898	1.121	1.239
Ni ₁ -Ni ₂ OP	0.116	0.049	0.075
4σ-Ni OP	0.121	0.125	0.121
5σ-Ni OP	0.482	0.473	0.500
2π _x -Ni OP	0.160	0.398	0.333
2π _y -Ni OP	0.160	0.169	0.333
electron occupation of 4σ	1.865	1.835	1.842
electron occupation of 5σ	1.587	1.563	1.554
electron occupation of 2π _x	0.316	0.612	0.505
electron occupation of 2π _y	0.316	0.381	0.505
Net charge on CO	-0.084	-0.392	-0.407

Table 8. Contribution of $2\pi_x$ and $2\pi_y$ to the C-O OP on Ni(111).

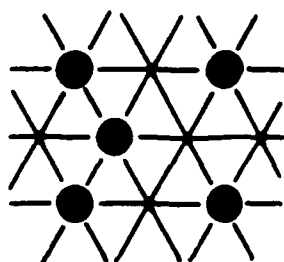
	$2\pi_x$	$2\pi_y$	total C-O OP
free CO	0	0	1.245
Ni(on-top)	-0.057	-0.057	1.105
Ni(2-fold)	-0.104	-0.062	1.016
Ni(3-fold)	-0.086	-0.086	1.009

Recall that the transformation of 3-fold site to 2-fold site is completed when $\theta \approx 0.16$. The average adsorbate-adsorbate distance at this coverage is around 6 Å. This interconversion should therefore be initiated by some long-range through-metal interaction. Simulation of this effect would require a large unit cell. We made no attempt to explain this experimental finding. Recent cluster calculations by ASED did point to Ni(3-fold) as the most stable site.^{58, 59}

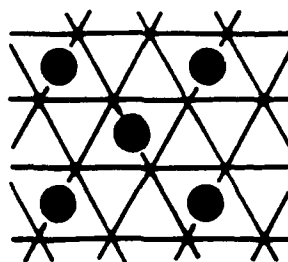
The two IR bands at 1804-1808 and 1814-1822 cm^{-1} have been tentatively assigned to the C-O stretching frequency at the hcp and fcc hollow site respectively by Chen et al.⁴⁷ The computed OP, 1.005 for the former; 1.009 for the latter, seems to agree with their conjecture.

Chemisorption at one-half coverage

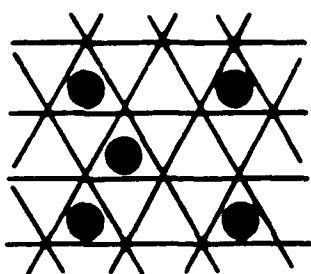
There are at least four surface structures compatible with the $c(4 \times 2)$ unit cell. They are sketched in 7 - 10. There are two adsorbate molecules per unit cell. For 7,



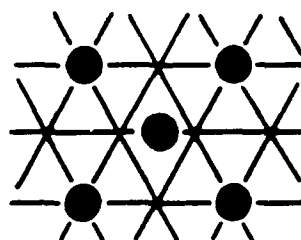
7



8



9



10

8 and 9, the adsorbate molecules are located at the on-top, 2-fold and fcc hollow site, respectively. In structure 10, half the CO are linearly bonded while the other are 2-fold bridging. For the first three cases, all the adsorbate molecules are symmetry-equivalent, due to a glide plane normal to the x-axis. When the incident and diffracted electron beam both lie in the glide plane, alternate beams along the glide plane, for which the indexing is odd, will be missing.^{60,61} Hence, in principle, the first three structures can be

distinguished from the last one by the systematic extinctions in their LEED patterns. If there is no increase in adsorbate-adsorbate interaction when θ changes from one-third to one-half, the most stable site for Ni(111), Pd(111) and Pt(111) would be **8**, **9** and **7** respectively. In practice, **8** is the experimentally preferred structure for Ni(111) and Pd(111) while **10** is favored on Pt(111).

Suppose a is the closest metal-metal contact at the surface. For the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, the shortest distance between neighboring CO molecules is $\sqrt{3}a$. Every surface atom bonds at most to one adsorbate molecule only. Hence there is little through-space or through-metal adsorbate-adsorbate interaction.

At one-half coverage, the shortest contacts between adsorbate molecules in **7** reduce to a . There would be an increase in through-space adsorbate-adsorbate repulsion, which is, however, calculated to be quite small, about 0.05 eV per CO molecule even for $a = 2.49 \text{ \AA}$, the nearest neighbor distance for Ni(111). In the case of **9**, besides the above direct repulsive interaction, one-half of the surface atoms have to bond to two adsorbate molecules, that is, there would be indirect through-metal interaction as well. For **8** and **10**, the adsorbate-adsorbate interaction is minimized.

In Figure 4 we display the DOS of the monolayer of CO (no metal surface here) arranged in the same geometry as the overlayer of **7** (or **9**), on Ni(111). The shapes of the bands, which are characteristic of the one-dimensional chain, clearly show that the interactions along the y -direction are much more important than those of the x -direction. The DOS for the corresponding monolayers for **8** and **10** are very similar. Thus only the former is presented in the next panel.

Figure 4 here

In summary, when θ increases from $1/3$ to $1/2$, there is a tendency for the linearly bonded and the 3-fold capped CO to convert partially or completely to the 2-fold bridged

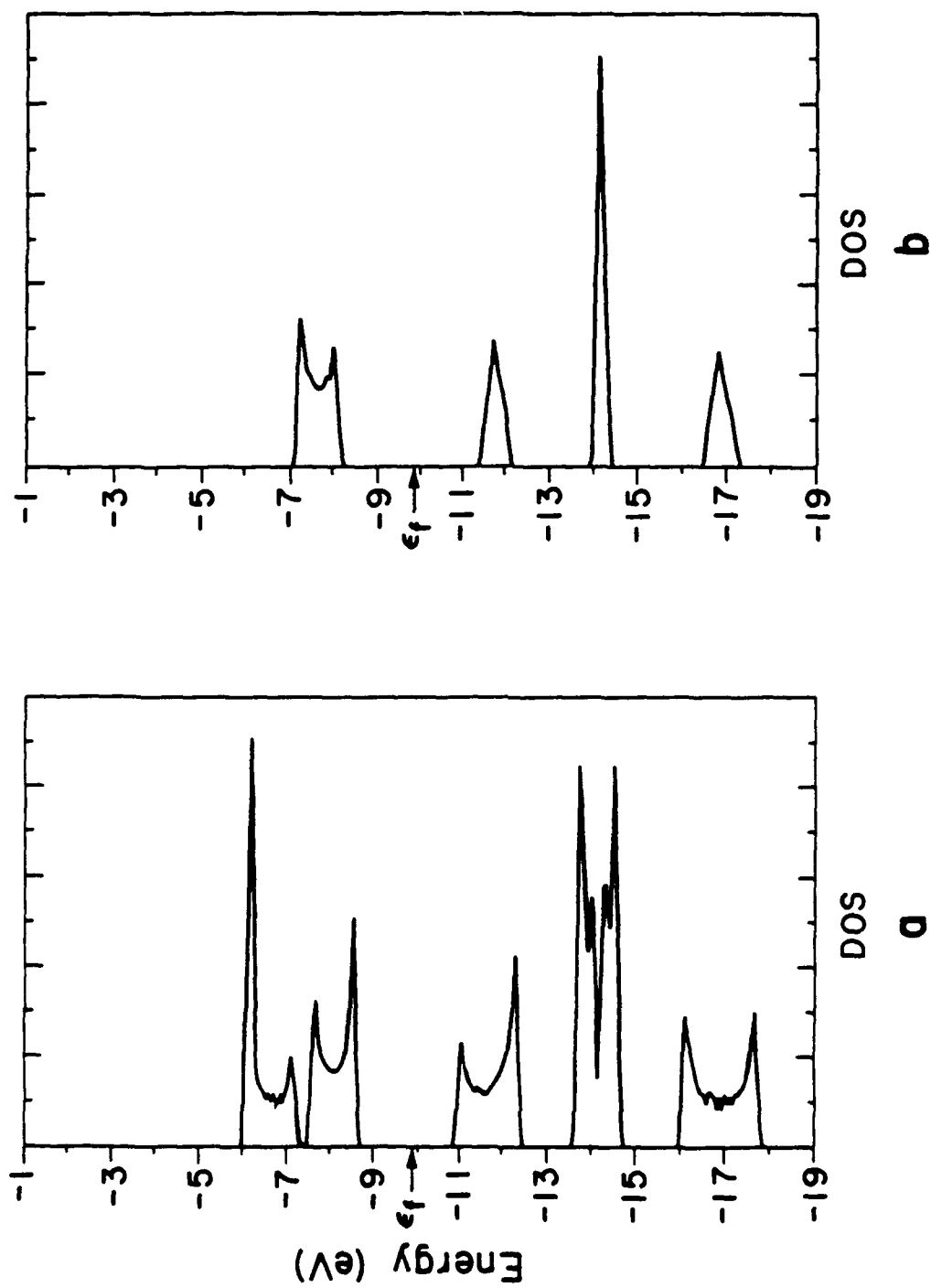


Figure 4. a) Total DOS of CO monolayer for structure 7.
b) Total DOS of CO monolayer for structure 8.

adsorbate. As shown by the binding energies in Table 9, the increase in adsorbate-adsorbate interactions seems to be able to trigger this transformation on Pt(111) and Pd(111). Since Ni(2-fold) is already the most stable site at one-third coverage, it survives when $\theta = 0.5$. Notice that only on Pt(111) has the exact geometry of the adsorbate molecules at one-half coverage been determined experimentally.²⁹ The results for the other two surfaces should, therefore, be treated with caution.

Table 9 here

Table 9. Binding Energies for Chemisorption at One-half Coverage.

Structure	Ni(111)	Pd(111)	Pt(111)
7	5.029	4.267	5.351
8	6.643	5.484	5.287
9	5.853	5.358	4.778
10	6.025	4.976	5.366

Comparison with Inverse Photoemission Spectra

There have been two inverse photoemission spectroscopy (IPES) studies for CO on Ni(111) at one-third coverage. In the first experiment, the unoccupied 2π states peak at 1.7 eV above the Fermi energy¹⁶ while in the second they are at about 3 eV.⁶² In Figure 5a, the total DOS of the $2\pi_x$ and $2\pi_y$ for Ni(2-fold) at one-third coverage is presented. The position of the empty 2π band fits the results of Frank et al. well.¹⁶

IPES has also been performed on Pd(111) and Pt(111) at one-third coverage.^{63,64} In the former case, the empty 2π states center at 4.0 eV above the Fermi energy, while in the latter case, it is 4.3 eV. A comparison between Figure 3a and Figure 5b suggests that the energy differences have been underestimated by more than 1 eV. Of course, inverse photoemission measurements actually involve complicated many-body interactions and may not be simply related to the energy difference between two orbitals.

For a given metal surface, one would expect that the stronger the adsorbate-surface bonding, the further will be the unoccupied 2π states pushed away from the Fermi energy by the d band. Interestingly, IPES seems to indicate the opposite.^{11,63} It has been proposed that the empty p_x and p_y orbitals of the metal may push down the 2π states.⁶⁵

Figure 5 here

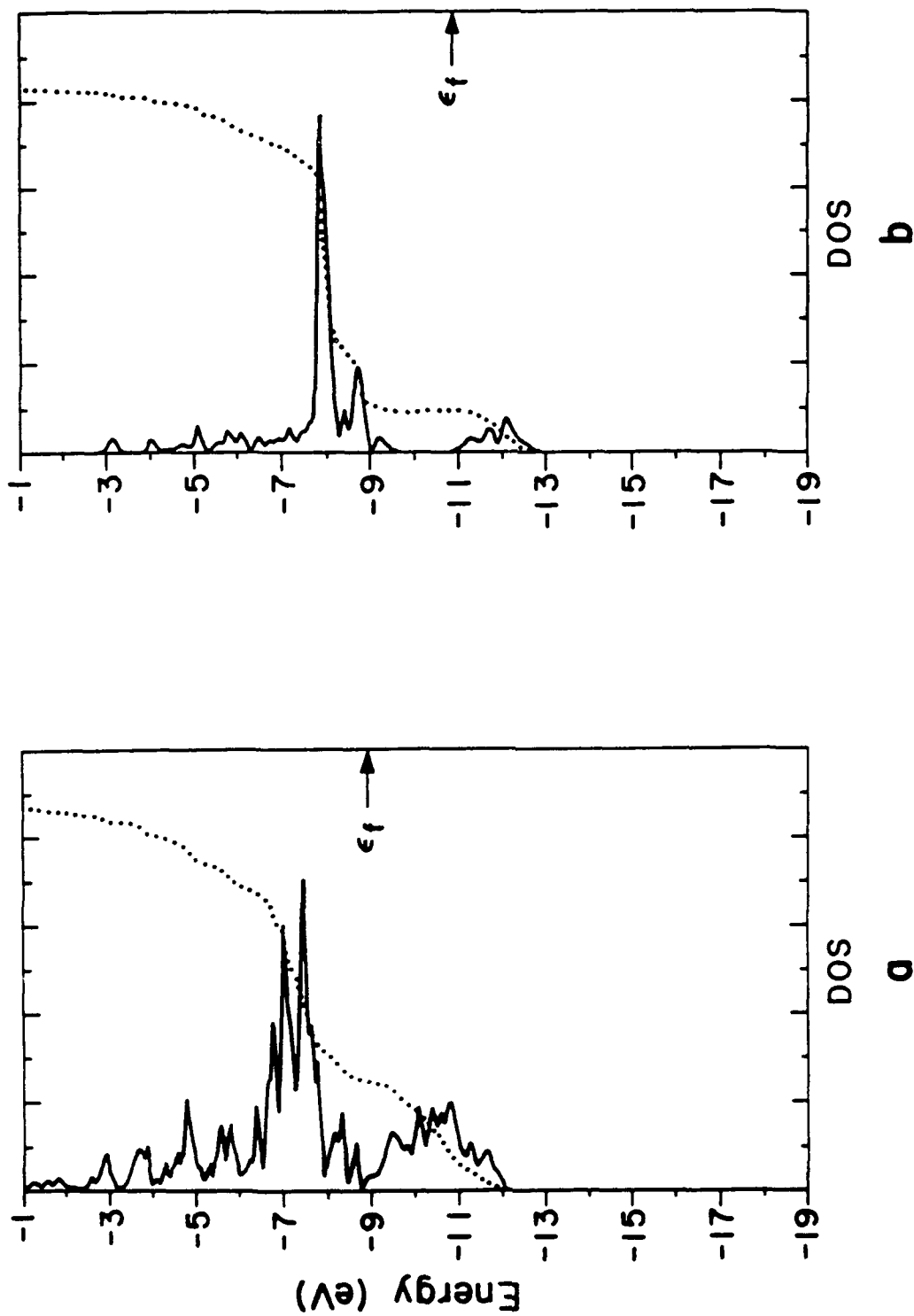


Figure 5. a) Total DOS of $2\pi_x$ and $2\pi_y$ for Ni(2-fold) at one-third coverage.
b) Total DOS of $2\pi_x$ and $2\pi_y$ for Pd(3-fold) at one-third coverage.

Final Remarks

Due to the better shielding of the 4f electrons, the effective nuclear charge acting on the 5d electrons of platinum is lower than that on the 4d electrons of palladium. The second, third, and fourth ionization potential (IP) of palladium atom are larger than the corresponding ones for platinum. The first IP of palladium atom involves the removal of a 4d electron. It is smaller than that of platinum, which is related to the ionization of a 6s electron.⁶⁶ The first IP's of these two metals, thus, do not indicate the relative energy of their d orbitals.⁶⁷ One of the consequences of the higher effective nuclear charge is that the palladium d band in solid metal is much narrower than that of platinum. Nickel forms carbonyl complexes readily. Palladium does so only reluctantly. Platinum is in-between in its bonding capability toward CO in discrete molecules. As pointed out by Hartley, the first atomic IP for nickel, palladium and platinum in the d^{10} configuration are 5.81, 8.33 and 8.20 eV, respectively.^{30,68} Hence, the tendency of the metal to donate d electron to the 2π orbitals in carbonyl complexes probably decreases in the order $Ni \gg Pt > Pd$. All these are in contrast to the usual periodic trends.

The work function ϕ of a metal consists of two parts. The first component originates from the surface dipole D , while the second portion is related to the bulk Fermi energy or chemical potential E_f of an electron:^{69,70}

$$\phi = D - E_f$$

The former depends on surface crystallographic orientation. Thus the work function for different crystal planes of the same metal can vary up to 0.8 eV. Similarly, the change in ϕ after adsorption, which usually ranges from 0.1 to 1.5 eV, can be attributed to change in D .⁶¹ The E_f , often termed the internal contribution to the work function, is determined solely by the bulk properties of the solid. It can be derived from band structure calculation. A higher E_f means more ready spilling out of electrons from the surface. This would lead to a larger D . The result of this feedback mechanism is that the work functions of pure metals usually lie between 2 to 6 eV.^{69,71} More remarkably, some metals such as nickel,

actually have a larger work function than that of carbon. A higher bulk Fermi energy, hence, need not imply a smaller work function and vice versa. In summary, the work function is a complicated object and should not be treated simply as the direct analogue of the atomic IP. The skeptical reader may consider the following example. The IP of the sodium atom, 5.14 eV, is greater than the work function of Ni(110), 5.04 eV. When sodium atoms are deposited on the Ni(110) surface, one would intuitively expect a small electron transfer from the surface to the half-filled 3s orbital of sodium atoms, were the work function and atomic IP on equal footing. In fact, at low coverage, all sodium atoms essentially lose their valence electrons to the surface.⁷²

The surface dipole layer, often called the double layer, has a thickness of the order of 2 to 3 Å. A simulation of the double layer, image potential and the Friedel oscillations of the electron density near the surface would require a metal slab of tens of atomic layers and the taking into account of all the relevant electrostatic interactions.^{71,73} This is currently beyond our computing capacity.

The extended Hückel method, and most cluster calculations, make no attempt to simulate the surface dipole. The Fermi energy for Ni(111), Pd(111) and Pt(111), using three-layer slabs as models, are computed to be -8.93, -11.04, and -9.90 eV respectively. These values, thus, bear no direct correspondence to the experimental work functions, which are 5.36, 5.6 and 5.7 eV, respectively.⁷¹ Although both relativistic augmented-plane-wave calculations and linear-muffin-tin orbitals method also indicate that the palladium Fermi energy is lower than that of platinum,⁷⁴ the metal-to- 2π back-donation of electron on Pd(111) may be underestimated. It is worthwhile to compare with other theoretical data.

The total electron populations of 1π and 2π of CO on palladium clusters have been obtained by a pseudopotential calculation.¹⁴ The occupation of 1π should be close to four. Hence, a reasonable lower bound for the the electron population of 2π deduced from this theoretical study for Pd(on-top), Pd(2-fold) and Pd(3-fold) are 0.142, 0.244 and 0.342 respectively, compared to 0.184, 0.331 and 0.358 in Table 6.

Conclusion

We have analyzed the adsorption of CO on Ni(111), Pd(111) and Pt(111), corresponding to the limit of strong chemisorption. The Blyholder model, simple and fruitful, is followed in general. Its major deficiency is the neglect of the 4σ orbital, which participates in the adsorbate-surface bonding. However, the interaction of the 5σ and the metal s and p_z band seems to be the most important ingredient of the bonding, as we see it. At the 2-fold or 3-fold bridge site, the s and p_z bands also interact substantially with the 2π orbitals.

The adsorbate-surface interaction tends to favor the 2-fold and 3-fold bridge site but the bond-weakening within the adsorbate and within the surface acts in the opposite direction. The site preferred results from a delicate balance between these two competing factors. Even a slight change in adsorbate-adsorbate interaction can change things around. The 2-fold site is more favored when the coverage increases from one-third to one-half.

Perhaps it is foolish to claim that our rough computations can resolve completely decades of controversies. The extended Hückel method, at its best, may only give the correct trends in bonding preferences and electron shift. Yet the absolute magnitudes of energetic quantities may be far afield. A comparison of the binding energies at various adsorption sites with the experimental chemisorption energies listed in this paper is sufficient to illustrate this point. We have tried to alleviate the problem of exaggerated electron flow by charge iteration. However, there is no guarantee that this is the perfect cure. Our calculations do not take entropy effects into account either. These may dominate,²¹ especially when the enthalpy change is small. The main objective of this work is to provide a detailed, and hopefully moderately reliable, picture of orbital interaction. This we think we have done.

Appendix

Tight-binding extended Hückel calculations, with a weighted H_{ij} approximation, have been applied throughout this paper.^{75,76} The geometrical assumptions concerning bond lengths (in Å) include the following: on Ni(111), C-O 1.13, Ni-Ni 2.49, Ni-C 1.71(on-top), 1.81(2-fold), and 1.96(3-fold); on Pd(111), C-O 1.15, Pd-Pd 2.75, Pd-C 1.82(on-top), 1.93(2-fold) and 2.05(3-fold); on Pt(111), C-O 1.15, Pt-Pt 2.77, Pt-C 1.85(on-top), 2.08(2-fold) and 2.23(3-fold). The extended Hückel parameters are listed in Table 10. Double zeta expansions of the metal d orbitals have been employed. The parameters of carbon monoxide are taken from previous studies.^{31,77} Charge iterations have been performed, assuming a quadratic dependence of metal H_{ii} 's on charge.⁷⁸

Table 10 here

The k points are generated according to the geometrical method of Böhm and Ramirez.⁷⁹ Since the energy differences between various adsorption sites of the same surface are expected to be small, 32 k point sets have been used for all calculations to ensure convergence. The irreducible wedges of the Brillouin zone for all the c(4x2) surface structures listed in this work are the same. Hence the errors in evaluating the energy differences among various adsorption sites at one-half coverage would be smaller.

The amount of work dedicated to the topic under discussion is enormous, scattered throughout the scientific literature of several decades. A complete survey in such a large domain is beyond our capabilities. We offer our sincere apologies for any omissions.

Table 10. Extended Hückel Parameters.

Atom	Orbital	H_{ii} (eV)	ζ_1	ζ_2	c_1	c_2
C	2s	-18.20	1.63			
	2p	-9.50	1.63			
O	2s	-29.60	2.27			
	2p	-13.60	2.27			
Ni	4s	-8.06	2.10			
	4p	-3.89	2.10			
	3d	-10.30	5.75	2.00	0.57	0.63
Pd	5s	-7.24	2.19			
	5p	-3.68	2.15			
	4d	-11.90	5.98	2.61	0.55	0.67
Pt	6s	-9.15	2.55			
	6p	-4.38	2.55			
	5d	-11.00	6.01	2.70	0.63	0.55

Acknowledgements

We thank Professor Norman Sheppard for pointing out this interesting problem to us. We are grateful to the Office of Naval Research for its support of this work. Acknowledgement is also made to Jane Jorgensen and Elisabeth Fields for their expert drawings.

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